

Long-term geochemical monitoring and extensive/compressive phenomena: case study of the Umbria Region (Central Apennines, Italy)

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Abstract

Long-term geochemical monitoring performed in the seismic area of the Umbria-Marche region of Italy (*i.e.* Central Apennines) has allowed us to create a model of the circulation of fluids and interpret the temporal chemical and isotopic variations of both the thermal springs as well as the gas vents. Coincident with the last seismic crisis, which struck the region in 1997-1998, an enhanced CO₂ degassing on a regional scale caused a *pH*-drop in all the thermal waters as a consequence of CO₂ dissolution. Furthermore, much higher ³He/⁴He isotope ratios pointed to a slight mantle-derived contribution. Radon activity increased to well above the $\pm 2\sigma$ interval of the earlier seismic period, after which it abruptly decreased to very low levels a few days before the occurrence of the single deep-located shock (March 26, 1998, 51 km deep). The anomalous CO₂ discharge was closely related to the extensional movement of the normal faults responsible for the *M_w* 5.7, 6.0 and 5.6 main shocks that characterized the earlier seismic phase. In contrast, a clear compressive sign is recognizable in the transient disappearance of the deep-originating components related to the *M_w* 5.3, 51 km-deep event that occurred on March 26, 1998. Anomalies were detected concomitantly with the seismicity, although they also occurred after the seismic crisis had terminated. We argue that the observed geochemical anomalies were driven by rock permeability changes induced by crustal deformations, and we describe how, in the absence of any release of elastic energy, the detection of anomalies reveals that a seismogenic process is developing. Indeed, comprehensive, long-term geochemical monitoring can provide new tools allowing us to better understand the development of seismogenesis.

Key words *geochemical monitoring – seismicity – helium – thermal waters*

1. Introduction

It is well-known that earthquakes can provoke modifications in the natural setting of a seismic

area and may induce modifications in the fluid phases, such as a decrease/increase in the water level of wells, changes in the temperature and/or chemical composition of the groundwaters, and variations both in the gas discharge flow-rates and in the chemical and isotopic composition of the gases (*e.g.*, see King, 1986; Thomas, 1988; Toutain and Boubrou, 1999). At times, precursor time and duration of the anomalies seem to increase as the magnitude and epicentral distance grow, but sometimes this is not the case. On the basis of previous observations carried out in several Italian seismic areas, some authors (Favara *et al.*, 2001; Italiano *et al.*, 2001, 2004; Caracausi

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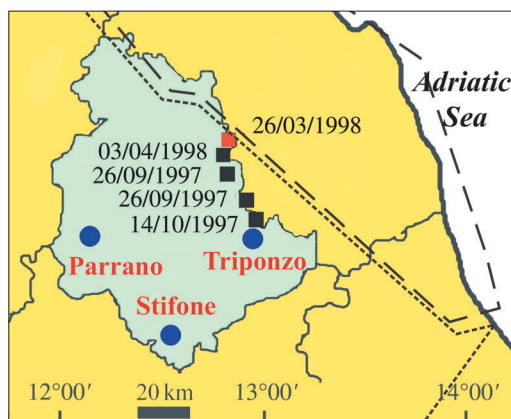


Fig. 1. Location of the selected sampling sites for thermal waters (Umbria Region, Central Italy) and the main boundaries between extensional and compressional zones of the Central Apennines (after Barba and Basili 2000). Squared symbols show the epicentral locations of the main shocks; in red the 26th March 1998 deep located event.

et al., 2002a,b) have suggested that the best way to approach the broad-ranging problem of fluid geochemistry and seismogenesis was to collect as many locally significant geochemical data as possible and to evaluate it within an interpretative geochemical model. Thus, the long-term geochemical monitoring of any seismic area enables us to define the background and detect any anomalies, which, besides the knowledge of fluid circulation and interaction, allow us to define the behaviour of these anomalies as a seismogenic process develops. Since the surface chemical/isotopic composition is a consequence of deep physical-chemical conditions and may change due to re-equilibrations at depth, the geodynamic context of the area may deeply influence the surface composition. In fact, shallow-originating fluids could mix with others coming from different depths of the crust and/or from the upper mantle. The mixing proportions may change with time due both to seasonal variations and/or to the development of seismogenesis (stress accumulation, deformation, strain release, etc.).

The seismic event in itself, however, is not the main goal of this research, although its forecasting does in some ways represent a sort of final target.

The monitoring activity focuses on the evaluation of the effects that the development of a seismogenic process has on the circulating fluids which may or may not generate a «seismic shock».

Starting from the beginning of the seismic crisis (September 26, 1997), thermal water samples (Bagni di Triponzo, Parrano and Stifone) and samples from gas vents (Montecastello di Vibio, Umbertide, San Faustino) were collected on a weekly basis during the period October 1997-July 1998 and at longer intervals thereafter (*i.e.* twice a week, then monthly and then once every season). The data collected during a rather quiet seismic period (1999-2002) allowed us to identify the background values for some geochemical parameters that could characterise the study area. All the values outside the $\pm 1\sigma$ interval were considered as being real variations. However, the observed fluctuations were wider than the $\pm 2\sigma$ interval.

Some previously published results have pointed out that: a) the thermal waters are Ca-SO_4^- enriched due to their circulation in the deep evaporitic basement and have changed their mixing proportions with cold waters typically equilibrated in shallow carbonate systems (Favara *et al.*, 2001); during the seismic period deep-originating waters contaminated shallow aquifers exploited for human purposes (Bazzoffia *et al.*, 2002); b) the gases dissolved in the thermal waters, CO_2 -dominated with the presence of CH_4 and an excess of N_2 in respect of the atmosphere, displayed various influxes of both deep-originating and atmospheric-derived components (Italiano *et al.*, 2004); the $^3\text{He}/^4\text{He}$ ratios of venting gases showed that although the region is located in a typical crustal environment, the contribution of a mantle-derived component could be detected (Italiano *et al.*, 2001).

This paper contains new data mainly collected at a single site, namely the thermal spring of Bagni di Triponzo, where the emitted fluids have undergone the widest geochemical modifications of all the monitored sites (*e.g.*, the temperature of the thermal water, $29.6 \pm 0.2^\circ\text{C}$ constant over time and with no seasonal effect, dropped by 2°C two weeks before and $> 20^\circ\text{C}$ two days before the occurrence of the March 26, 1998 shock). This paper focuses on the relationships between the geochemistry of the circulating fluids and the mechanical properties of the hosting

rocks, highlighting the geochemical phenomena related to extension *versus* those related to the compressive behaviour of the faults involved.

2. Seismic activity and geotectonic settings

The Umbria Apennine is affected by frequent seismic activity associated with an extensional strain field. Earthquakes affecting the area generally occur in the sedimentary cover at a shallow depth (Deschamps *et al.*, 1984; Haessler *et al.*, 1988). At least 22 $M_I \leq 5$ local earthquakes occurred between 1279 and 1984 (Boschi *et al.*, 1998). Focal mechanisms of the main shocks occurred in 1979, 1984 and 1997. This has also been confirmed by further stress indicators (Montone *et al.*, 1997), highlighting the active extension processes in the crust characterized by NE-SW and E-W directions (Frepoli and Amato, 1997; Amato *et al.*, 1998). Selvaggi and Amato (1992) demonstrated that deep subcrustal seismicity also affects the Central and Northern Apennines. Subcrustal seismicity may indicate the ongoing activity of subductive processes.

After a relatively long period of quiescence, a seismic swarm, marked by the M_I 4.5 Massa Martana mainshock, occurred in the Umbria Region in May 1997 about 40 km south of the village of «Colfiorito», which was the area most damaged during the subsequent months of September and October 1997. The strongest event, which occurred in 1998 (M_I 5.7 on March 26), had a subcrustal hypocenter located at a depth of about 51 kms (Morelli *et al.*, 2000). A descending lithospheric slab, linked to an ongoing subduction process, may account for subcrustal events in the Northern-Central Apennines (Selvaggi and Amato, 1992). The entire seismogenic process caused a crustal deformation with a maximum horizontal co-seismic displacement of 14 ± 1.8 cm and a maximum co-seismic subsidence of 24 ± 3 cm. These were detected by means of SAR differential interferometry and GPS data (Stramondo *et al.*, 1999), while a post-seismic long-term deformation process was detected by means of levelling data (Basili and Meghraoui, 2001).

The inner part of the Umbria-Marche Apennine was affected by a relatively extensional

regime able to generate a set of grabens during Plio-Pleistocene times within the frame of a possible, limited rifting process (Elter *et al.*, 1975; Liotta *et al.*, 1998).

The basement of the Central Apenninic rock is made up of phyllitic rocks from the Carboniferous age, underlying conglomerates of the Verucano Group attributable to the Middle Triassic age. The sedimentary cover continues with the Burano anhydrites, Contorta limestone and Calcare Massiccio (Late Triassic-Early Lias). It is followed by a pelagic, calcareous and marly multilayer (middle Lias-Oligocene) and ends in a flisch sequence (Middle to Upper Pliocene) (Bally *et al.*, 1986; Ponziani *et al.*, 1995).

Travertine rocks occur in the vicinity of CO₂ gas emissions of the Umbria Apennine, evidencing the ascent of deep fluids towards the surface (Barbier and Fanelli, 1976). CO₂ emissions are widely distributed across the Umbria Region and can be related to the slightly anomalous heat flow pattern (Cataldi *et al.*, 1995), that may be responsible for the thermo-metamorphic processes at depth (Chiodini *et al.*, 1999), while intense local faulting (*e.g.*, Cello *et al.*, 1997) can be considered responsible for CO₂ uprising. The existence of the magmatic structures of San Venanzo (Stoppa and Sforna, 1995) in the vicinity of Montecastello di Vibio, and Colle Fabbri (Stoppa, 1988) in the vicinity of Massa Martana, provides clues to the possible increase in local crustal permeability.

The Triponto spring sources are located in a limestone formation (Calcare Massiccio) of the Hettangian-Sinemurian age characterized by high porosity. This favours locally important karst phenomena. Spring sources are located at the bottom of a canyon generated by an important regional fault, which cut the limestone formations allowing the groundwaters to reach the underlying evaporitic rocks (Giachino *et al.*, 1991).

3. Sampling and analytical methods

Water composition was determined by both field measurements (temperature, pH, electrical conductivity and Rn activity) and

laboratory analyses. In the field the radon activity was measured by an EDA-RD 200 Radon detector. A 130-ml aliquot of water was degassed and the extracted Radon was measured in a ZnS (silver activated) coated cell. The analytical errors have been estimated to be $\pm 10\%$. The temperature was always measured using the same mercury thermometer (scale 0-50°C; resolution 0.1°C), while *pH* and conductivity were measured by electronic instruments calibrated *in situ* using buffer solutions (error below $\pm 5\%$). The chemical composition was determined by High-Pressure Liquid Chromatography (HPLC, Dionex 2001) using a Dionex CS-12 and a Dionex AS4A-SC column for cation and anion determinations, respectively. The HCO_3^- content was measured in the laboratory by standard titration procedures on samples sealed in the field following the same method for the dissolved gas analyses.

For the analysis of the dissolved gases, samples were collected and sealed in the field in 240 ml Pyrex bottles. Keeping the bottles immersed, they were filled with the thermal water, and then a gas-tight septum was fitted on using special pliers.

The chemical gas-analyses were carried out using the methodology based on the equilibrium partitioning of gases between the liquid and gas phase (Sugisaki and Taki, 1987), and following the procedure previously suggested by Capasso and Inguaggiato (1998). The chemical analyses and helium isotope measurements were made by gas-chromatography and mass spectrometry, respectively; the sample was split into two gas aliquots concomitantly extracted from the same sampling bottle (Italiano *et al.*, 2004). Chemical analyses of He , O_2 , N_2 , CH_4 and CO_2 were carried out using a Perkin Elmer 8500 gas-chromatograph equipped with a 4 m Carbosieve 5A column and double detector (Flame Ionization Detector with methanizer and Hot Wire Detector). The detection limits were 5 ppmv for He , O_2 , and N_2 , and 1 ppmv for CH_4 and CO_2 . Analytical errors were $\pm 5\%$ for He , and $\pm 3\%$ for the other species.

A 0.3 cm³ aliquot was admitted at a known pressure to the purification UHV line for helium isotope analysis. Helium was purified in

three stages in separate sections of an all-metal UHV preparation system. First, the reactive gases were adsorbed into a charcoal trap held at 77 K; then two SAES getters worked simultaneously to adsorb residual nitrogen at 250°C and hydrogen at room temperature. The third step, after measuring the $^4\text{He}/^{20}\text{Ne}$ ratio and checking for residual ^{40}Ar on an in-line Quadrupole Mass Spectrometer (QMS, VG Quartz), was to completely separate helium from neon by means of a charcoal trap held at 40 K. The isotopic analyses of the purified helium fraction were performed with a modified static vacuum mass spectrometer (VG5400TFT, VG Isotopes) that allows for the simultaneous detection of ^3He and ^4He -ion beams, reducing the $^3\text{He}/^4\text{He}$ measurement error to very low values. Typical uncertainties in the range of low- ^3He (radiogenic) samples are below $\pm 5\%$.

4. Results and discussions

The chemical composition of the sampled thermal waters was established to be a mixture of a carbonate component, equilibrated with calcite and dolomite, and a selenitic component circulating in the Evaporitic Triassic basement (Chiodini *et al.*, 1982, 1999; Quattrocchi *et al.*, 2000). However, no information was available regarding temporal modifications before the occurrence of the last seismic crisis (Favara *et al.*, 2001). The Langelier-Ludwig diagram (Langelier and Ludwig, 1942) in fig. 2 highlights the composition changes of the major constituents during the seismic crisis. It should be noted that not only did the composition change, but the physical-chemical features and the flow rate of the thermal waters did as well (Favara *et al.*, 2001; see also fig. 7). Figures 3 and 4a,b show both the background anomalies and the recorded ones for some anions and cations of the investigated springs (Favara *et al.*, 2001; Caracausi *et al.*, 2002a).

Using the WATEQP software (Appelo, 1988) we were able to calculate the Saturation Index (SI) expressed as the logarithm of the ion activity ratio, pertinent to a mineralogical phase, and the equilibrium constant of its solubility product. The results plotted in figs. 5a,b and 6 show the water-

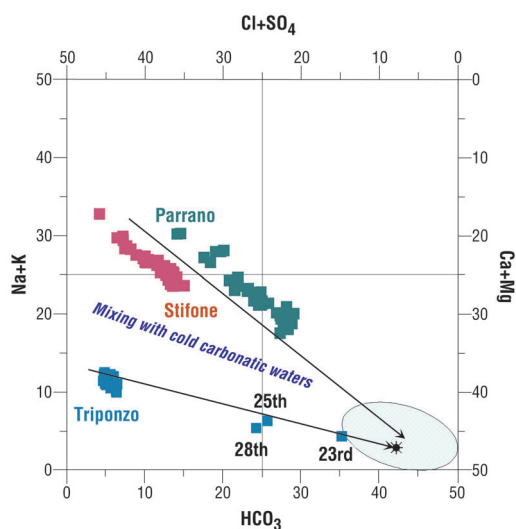


Fig. 2. Langelier-Ludwig classification diagram. The plotted analyses show the modifications that occurred over time at all the selected thermal springs. The dates show the modifications that happened at Triponzo at the end of March 1998. The arrows display the chemical modifications caused by cold water mixing. Concentration units are in mEq/l.

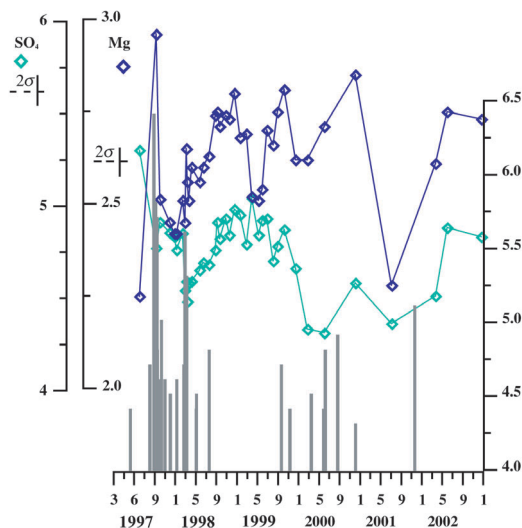


Fig. 3. Temporal variation of SO_4 and Mg concentration (mEq/l) at the thermal spring of Parrano between June 1997 and June 2002. The occurrence of seismic events with $M_I > 4$ is reported as a bar diagram.

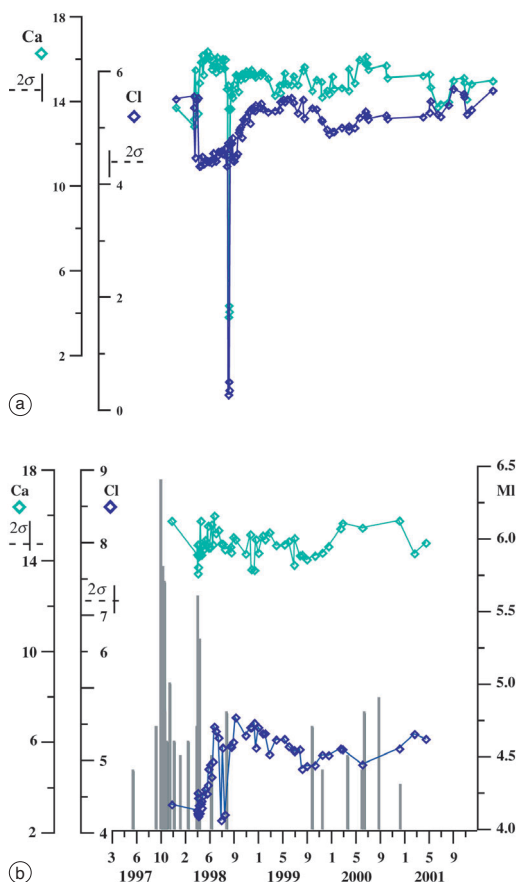


Fig. 4a,b. Temporal variation of Ca and Cl concentration (mEq/l) at the thermal springs of Triponzo «pipe» and «pond» between June 1997 and December 2001 and their relationship to the seismicity as shown by the associated bar diagram. Even though the two springs are located several dozen meters apart at the same thermal area, they followed very different trends during the monitoring period. The «pipe» spring is the one referred to by Favara *et al.* (2001), while the «pond» site is the one sampled by Quattrocchi *et al.* (2000).

rock interactions occurring at the thermal waters of Parrano Stifone and Triponzo, respectively.

All the Calcite-Dolomite SI show that the discharged thermal waters are normally from under-saturated to close-to-saturation with respect to both of the two mineralogical species,

as this variability is related to seasonal variations. However, they varied simultaneously as time passed (figs. 5a,b and 6) to become decisively under-saturated over a short time-scale. The Calcite-Dolomite SI pattern is similar for all the thermal waters, but Parrano and Stifone (fig. 5a,b) show variable SI even for gypsum. These results are consistent with an initial equilibration within evaporitic (selenitic) reservoirs, then thermal waters mix with shallower cold waters equilibrated in carbonatic reservoirs during their uprising towards the surface.

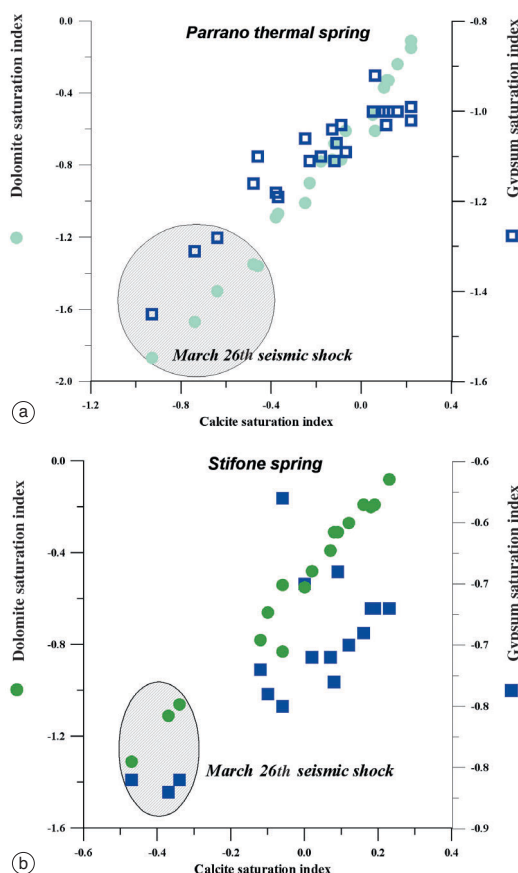


Fig. 5a,b. Calcite versus Dolomite and Calcite-Gypsum Saturation Indices (SI) calculated for the thermal springs of Parrano (a) and Stifone (b). The lowest SI are related to the event that occurred in March 1998.

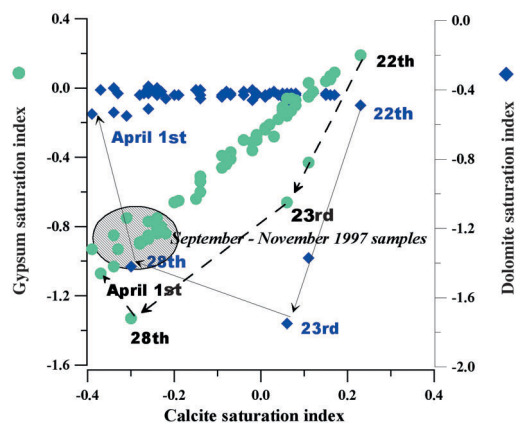


Fig. 6. Saturation indices calculated for the thermal water samples of Triponzo «pipe». The faulting behaviour that marked the seismic events of September-October 1997 and March 1998, respectively, induced significant and different effects that can be recognized in the paths followed by the water-bodies when returning to initial conditions, *i.e.* chemical equilibrium. The dates refer to the month of March 1998.

All the sampled thermal waters displayed the lowest SI values during the earlier phase of the seismic crisis (September-October 1997), in agreement with the extension that marked the faulting activity. Then the SI increased as time passed.

Normal faulting (Barba and Basili, 2000) increased crustal permeability allowing a higher CO_2 flow rate to the surface (Heinicke *et al.*, 2000; Italiano *et al.*, 2001), thus inducing a higher aqueous CO_2 concentration in the thermal waters. As a consequence of this, the aggressiveness of the groundwaters increased, thereby causing more limestone to dissolve. However, considering the chemical reaction kinetics, the equilibrium with the hosting rocks was far from being achieved and the calculated SI displayed a water-body that became less and less under-saturated in both calcite and dolomite (fig. 6). The evidence that the gypsum saturation index and the emission temperature remained unchanged means that the crustal permeability increase did not enhance the thermal waters uprising from the Evaporitic basement. The gypsum SI at Triponzo shows that the water is constantly gypsum-un-

der-saturated with ($SI = -0.4$). Furthermore, the calcite SI is close to saturation and varies as time passes (fig. 6). The thermal water from Triponzo showed the highest calcite and dolomite SI in the sample collected four days before 26th March, $M_I = 5.7$, deep located event (Morelli *et al.*, 2000). The water samples taken during the days that followed showed some very interesting behaviour: all the calcite and dolomite SI dropped to typical under-saturated values, whereas the sample taken on 1st April was again in the range recorded at the beginning of the seismic crisis. Since the observed modifications were consistent with other observations that denoted a transient disappearance of the thermal water component (Favara *et al.*, 2001), they reveal a compressive phenomenon that involved various crustal layers. The compression was already acting on the deep crustal layers many days before the seismic shock, obstructing the rise of CO_2 . The water sample dated 22nd March shows a decrease in the dissolved CO_2 that modified the equilibrium conditions of the water body toward lower SI values. The samples taken in the days that followed exhibit a trend toward a new chemical equilibrium, with a wider decrease in the dolomite SI in respect of the calcite SI. The sample collected on the 28th, two days after the shock, shows the lowest SI for both the mineralogical species. The trend in gypsum-calcite SI (fig. 6) highlights another aspect of the compressive mechanism: gypsum SI did not change very much before the earthquake, however afterwards it displayed the lowest value (sample dated 28th March). This is related to the transient disappearance of the thermal water component, as pointed out by the dramatic water temperature drop, meaning that the compression obstructed the uprising pathways located at the level of the evaporitic basement (where waters become «thermal») at the end of the compression. An alternative explanation, based on the occurrence of mixing phenomena, has to be ruled out due to the very low temperature ($8.4^\circ C$) reached by the thermal waters that cannot be a mixture of a thermal component, having a temperature of about $30^\circ C$, with water colder than the infiltrating waters (normally as cold as $8-10^\circ C$).

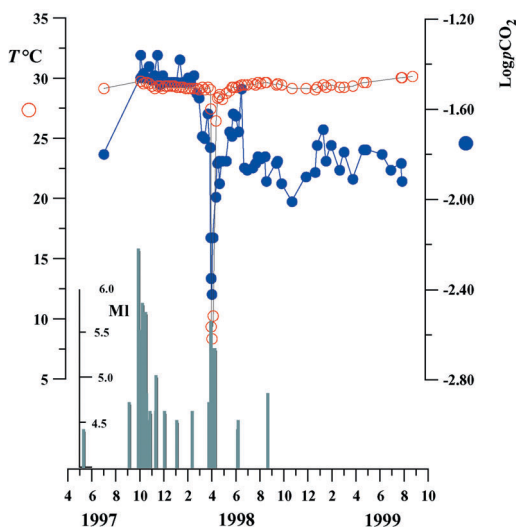


Fig. 7. $\log pCO_2$, temperature and seismicity versus time at the Triponzo «pipe» spring. Data refer to the sampling period that lasted from June 1997 to August 1999.

The graph \log pressure CO_2 versus temperature (fig. 7) shows that, two weeks before 26th March seismic shock, the thermal component was already mixing with cold waters or, alternatively, that the relative flow-rates were changing. The $20^\circ C$ drop occurred two days before the shock and the time the temperature took to return to the same pre-seismic range (*i.e.* some months) is consistent with a long-lasting process (compression and relaxation).

Figure 8 shows the radon activity trend versus pH . The different behaviour of Rn at the times of the two seismic periods in 1997 and 1998 is clearly evident. In fact, during the former, Rn increased, reaching its peak activity, while, coincident with the latter, it decreased to its lowest value. The activity of Rn returned to background values about 15 weeks after the remarkable geochemical changes observed in concomitance with the last, deep seismic shock (March 1998).

The pH variation pattern is similar, although antithetical. A 0.3 pH -unit decrease, that lasted for 6 months, was observed at the

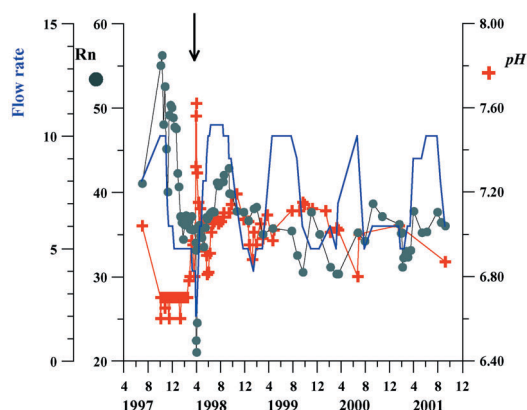


Fig. 8. Radon activity (Bq/l), flow-rate (litres per second) and pH versus time at Triponzo «pipe» thermal spring. The flow rate changes because of seasonal effects but does not affect the radon activity, the pH or the temperature (see fig. 7). In coincidence with the deep event of 26th March 1998, both the flow rate and radon concentration dropped to the lowest values ever recorded (see text).

beginning of the seismic crisis. The values of pH increased towards the pre-seismic/background values at the end of February 1998, and exhibited a further, sudden increase of the order of 0.8 units in concomitance with the lowest radon activity, the lowest water temperature and flow-rate, and the highest $^3\text{He}/^4\text{He}$ ratio (*i.e.* the variations related to the 26th March 1998 shock). It then went back to within the $\pm 2\sigma$ background interval, displaying variations, probably due to seasonal oscillations, consistent with those of Rn, $p\text{CO}_2$, etc.

Rn and water flow rate followed very similar trends (fig. 8) that occurred at an almost constant water temperature (apart from the 20°C -drop preceding the 26th March 1998 seismic event). The absence of significant flow-rate-related temperature variations implies that local hydrological settings control the flow rate, thus its temporal variation does not represent variable mixing proportions between the deep selenitic thermal component and the shallow cold, carbonatic water, but variable hydrostatic loads.

Since the mixing ratios of the thermal water are almost the same on a temporal scale, the pH

decrease recorded at the beginning of the seismic crisis cannot be related to compositional variations but to the massive CO_2 output in the area. This evidence leads to the consideration that at the beginning of the seismic crisis the excess radon release was triggered by the CO_2 outflow (*i.e.* Dongarrà and Martinelli, 1995 and references therein). Rn reached its lowest value when only the carbonatic water was outflowing, highlighting how the background of this noble gas is kept at levels of about 40 Bq/l by the thermal component.

Figure 9 shows the inverse correlation between the trends of the radon activity and the $^3\text{He}/^4\text{He}$ isotope ratio. This pattern, that gives support to the hypothesis of an enhanced crustal permeability that allowed CO_2 to be released and to act as carrier for the heavy, low-mobile radon, highlights the same radi-

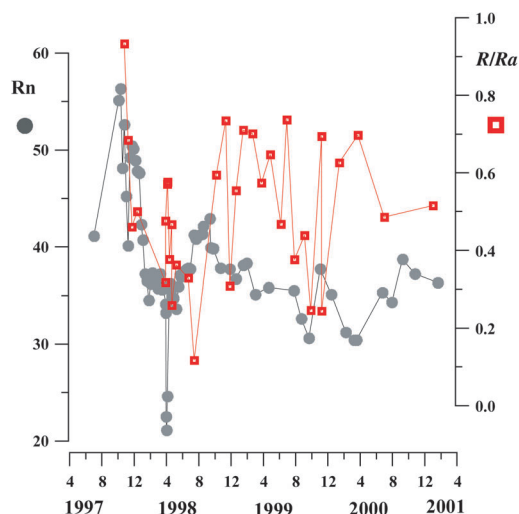


Fig. 9. Radon activity (Bq/l) and $^3\text{He}/^4\text{He}$ isotope ratio in the thermal water of Triponzo «pipe». During the March 1998 seismicity the radon activity displayed a marked antithetical trend in respect of the $^3\text{He}/^4\text{He}$ ratio, showing that radon content and ^4He are related to a common radiogenic origin. The increase in the R/Ra values is a consequence of the dissolution of an atmospheric component in the thermal waters. The displayed helium isotope ratios, expressed as R/Ra values (R = sample ratio; Ra = atmospheric ratio = 1.39×10^{-6}), have not been corrected for atmospheric contamination.

ogenic origin for ^4He and Rn: they both originate from the deep crustal levels involved in the tensile and compressive phenomena of the seismogenic process.

5. Conclusions

The long-term monitoring program, which started in July 1997, allowed us to interpret the geochemical information in such a way as to model the circulation pattern of the fluids released in the area. Geochemical variations disclosed changes in crustal permeability that are to be referred to deformations associated with subductive processes that characterize the Apennine chain. The most significant geochemical changes were apparently linked to 5 events characterized by $M_I \leq 5$ and limited to the period September 1997-April 1998; conversely the long-term geochemical trends show the persistence of long-lasting processes that have no relationship with the seismic shocks. The results collected reasonably denote extensive crustal movements at the beginning of the seismic crisis, in full agreement with the observations that the normal fault, known as Colfiorito Fault, was the first structure to move (Basili and Barba, 2000). The enhanced CO_2 release was one of the consequences that induced modifications in the chemical equilibrium of the water bodies. Coincident with the 51 km-deep seismic shock that occurred on 26th March 1998, a dramatic permeability drop, capable of modifying the deep thermal water circuit, was responsible for the most extensive modifications observed during the entire seismic crisis. Nevertheless the focal mechanism of the event was a combination of normal faulting and strike-slip (Morelli *et al.*, 2000), whereas the observed geochemical modifications reveal an opposite effect at shallower levels. It is worth noting that the variations occurred some days before and continued some days after the event, thereby supporting the hypothesis that the permeability drop was not a consequence of the earthquake itself.

Some strong geochemical variations also occurred in the period May-August 1998, when there was only one significant event ($M_I \geq 4.8$, August

15th, 1998), the epicentre of which was located about 80 km southwards, on the same main tectonic structure. The results show that the geochemistry of the fluids in a seismic area reflects the faulting behaviour and the properties of the hosting rocks, so it is closely related to the local tectonic, geologic and hydrologic settings, and that the findings collected in one selected area cannot be applied directly to another. Taking into consideration all the results we obtained, we argue that the geochemical variations are linked to a more general seismogenic process, involving crustal deformation, rather than to single events. The results strongly outline that without long-term geochemical monitoring, it is impossible either to interpret or to create a model of the geochemical anomalies and the temporal variations occurring during the development of a seismogenic process.

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